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INFLUENCE OF MODERN COAL-FIRED POWER TECHNOLOGIES ON FLY ASH PROPERTIES AND USE IN CONCRETE

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Influence of Modern Coal-fired Power Technologies on Fly Ash Properties and Use in Concrete

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Abstract

The Paper investigates the properties and use of fly ash produced from technologies developed to reduce environmental impact/improve efficiency of the coal-fired power generation process. These include, NO_x reduction, co-combustion, supercritical steam technology and oxy-fuel combustion. The nine samples examined were characterized physically, chemically and in terms of their reactivity. Tests were also carried out for consistence and compressive strength of concrete. Comparisons were made with (i) a selection of reference fly ashes, (ii) the requirements of EN 450-1 and (iii) fly ash studies from the 1980s and 1990s. The results indicate that for some processes, fly ash tended to be coarser and of higher loss-on-ignition (co-combustion and in-combustion NO_x reduction), while for others lower carbon contents were found (supercritical steam), or there was little obvious effect. Fly ash chemistry was slightly affected in some cases, but mainly as expected for the coal being used. There was general agreement between water requirement and activity index with fly ash fineness. Similar effects were noted with concrete in terms of superplasticizing admixture dose for a target slump and compressive strength. The behaviour of the materials was similar to that from the earlier studies and suggests suitability for use in concrete construction.

INTRODUCTION

Electricity generation by firing coal has been carried out for more than 100 years (Breeze, 2015). This period has seen technical changes, developments in electricity networks, and industry re-structuring (Clarke, 2015). More recently, concerns have been expressed about environmental impact (Deutch and Lester, 2004) and electricity is increasingly being generated by other means (Department for Business, Energy and Industrial Strategy, 2017). Similarly, efforts have focussed on implementing technologies that improve efficiency and/or reduce emissions associated with coal-firing (Buhre et al., 2005; Beer, 2007; Franco and Diaz, 2009). It is, therefore, likely that fly ash, the construction resource from the process, will be increasingly produced from these modern techniques.

Modern coal-fired power technologies can be generally divided into four groups: (i) **NO_x reduction methods** operate either (a) by converting NO_x to N₂ (post-combustion), using a reducing agent (commonly ammonia or urea), either with a catalyst, frequently a base metal oxide, (selective catalytic reduction (SCR)), or without (selective non-catalytic reduction (SNCR)), or (b) by altering combustion chamber conditions (in-combustion; normally the availability of fuel/air, and temperature) and thereby NO_x levels. (ii) **Co-combustion** involves burning coal with other organic materials (co-fuels), e.g. wood chips or petroleum coke, typically at low to moderate levels. This uses renewable or waste materials, conserves coal and offers potential benefits for emissions. (iii) **Supercritical technology** uses supercritical steam cycles, improving generation efficiency, also reducing coal requirements and emissions. The system hardware usually comprises high strength alloys for the

temperatures and pressures involved. (iv) **Oxy-fuel combustion** replaces combustion chamber air with oxygen. The flue gases mainly comprise CO₂ and water, with capture of the former likely to be part of the process. A portion of the flue gases is often recycled to dilute oxygen and regulate temperature.

Literature on fly ash from these technologies indicates that there is some information on (i) and (ii), but less is available for (iii) and (iv). Studies suggest for (i) that while post-combustion measures tend to have little effect on fly ash (although ammonia may be present; Rathbone and Robl, 2002), in-combustion NO_x reduction (e.g. low NO_x burners) can lead to coarsening and increased carbon contents (Maier et al., 1994; Hower et al., 1997). For (ii) behaviour appears to be fuel-dependent, with some influences on physical and chemical properties generally noted (van den Berg et al, 2001; Sarab  r, 2014). In the case of (iii), reductions in carbon may occur depending on the combustion/other systems used with the technology (Sato et al., 2001; Watanabe et al., 2004), while for (iv) pilot-scale furnace experiments suggest small changes in fly ash properties (Wall et al., 2009), although higher sulfate levels have been noted, reflecting flue gas recycling (Scheffknecht et al., 2011).

Limited research on mortar/concrete suggests some influences corresponding to fly ash characteristics. For example, with the effects on fly ash for (i) (in-combustion NO_x reduction) and (ii) noted above, greater water and air-entraining admixture requirements have been found (Fox and Constantinier, 2007; Wang et al., 2008). Data for hardened properties indicate reductions in compressive strength for (i) (Fox and Constantinier, 2007), with similar effects or minor differences noted for (ii) (with various co-fuels); Scott and Thomas, 2007; Johnson et al., 2010; Sarab  r, 2014). Little or no research for fly ashes from (iii) and (iv) in mortar/concrete appears to have been carried out. Given these developments and limited information in some cases, a study was set up to investigate the influence of modern coal-fired power technologies on the resulting fly ashes and their use in concrete.

PROGRAMME OF WORK

Initial studies investigated fly ash characteristics, with nine modern test materials examined. As sourcing of the fly ashes before and after introduction of the new coal-fired power technologies was not possible, they were evaluated with respect to (i) three (reference) fly ashes and (ii) the requirements of the appropriate Standard covering the material, EN 450-1 (BSI, 2012). Experiments examining physical and chemical properties, and reactivity were carried out.

The study progressed to examine the fly ashes in concrete (using two w/c ratios) and their influences on fresh properties (superplasticizing admixture (SP) dose for target slump) and compressive strength development (100 mm cube). Additional concretes were used to investigate potential water savings with selective fly ashes and their effects on compressive strength. To assist the data interpretation, scanning electron microscopy (SEM) studies were carried out. Comparisons were also made with research from the 1980s and 1990s, considering fly ashes produced during these periods (Dhir et al., 1985; Dhir et al., 1996), where appropriate.

MATERIALS

Fly Ashes

A range of UK/EU fly ashes, originating from bituminous coal, unless noted otherwise, and following dry storage were obtained for the study, as shown in Table 1. Most power stations use NO_x reducing methods and hence the fly ashes studied were, in some cases, from a combination of these and the other techniques being investigated. FA1 to 3, covering a range of fineness and of low loss-on-ignition (LOI), were taken as reference materials. FA1 was from a power station operating at full capacity (base load), while FA2 was a commercially available Category S fly ash to EN 450-1 (BSI, 2012), with FA3 an older material from the 1990s.

FA4 to 6 were produced using specific NO_x reduction methods, with FA4 and 5 from stations with SCR and SNCR (i.e. post-combustion) and FA6 from an in-combustion natural gas re-burn system, converting NO_x to nitrogen and water. FA7 to 9 used co-combustion, with FA7 and 8 (from a power station burning anthracite coal), sampled in winter and summer, adopting wood chips as the co-fuel, and FA9 petroleum coke. The former also has ammonia injected to assist collection at the precipitators. FA10 and 11 were from power stations with supercritical steam technology, while FA12 was an oxy-fuel fly ash from a 1 MW trial burning unit.

Other Materials

A Portland cement (PC), Strength Class 52.5 N to EN 197-1 (BSI, 2011a), was used in the mortars and concretes. Standard sand to EN 196-1 (BSI, 2016) was adopted for water requirement and activity index tests. The aggregates for concrete (laboratory-dried before use), conformed to EN 12620 (BSI, 2002) and comprised 10/20 mm and 4/10 mm gravel and a 0/4 mm sand, with particle densities 2610, 2600 and 2630 kg/m³ and water absorptions (laboratory dry to saturated surface dry) 1.3, 1.4 and 0.8%, respectively. A SP to EN 934-2 (BSI, 2009), based on a modified polycarboxylic ether, was used in the concretes.

EXPERIMENTAL DETAILS

Fly Ash Characteristics

Fly ash fineness tests followed EN 451-2 (BSI, 1995) and involved wet-sieving 1.0 g of material under a water sprinkler, at fixed pressure, for 1 minute (45 μm mesh). The mass retained after oven-drying was expressed as a percentage of dry fly ash, with repeats made until a difference of $\leq 0.3\%$ was obtained. Particle size distribution was also measured by Malvern Mastersizer2000 LASER analyser, based on light diffraction after passing through a suspension of the sample.

The LOI of fly ash was tested by igniting 1.0 g of sample at 975°C for 1 hour, as described in EN 450-1 (BSI, 2012). The LOI was the percentage mass loss with respect to the original fly ash mass, based on two tests per sample. Specific surface area measurements by nitrogen adsorption (BET) and foam index tests (with sodium dodecyl benzene sulfonate surfactant) as described previously (McCarthy et al., 2012) were made to provide an indication of the carbon characteristics and influences on air-entrainment.

Measurements of fly ash colour were carried out on powder samples compressed against a glass plate using a CR-210 Minolta Chromameter. The results were obtained in terms of the CIE (International Commission on Illumination) $L^*a^*b^*$ colour system. For fly ash, a^* and b^* (red/green and yellow/blue) are near zero (given their grey colour) and the results are presented as lightness (L) values.

The bulk oxide composition was determined on pressed powder pellets with a Philips PW2424 sequential X-ray fluorescence spectrometer and $\text{RhK}\alpha$ source, calibrated against international standards. Mineralogy was tested using a Hilton-Brooks X-ray diffractometer with monochromatic $\text{CuK}\alpha$ source and curved graphite single crystal chrometer (40 kV, 30 mA). The samples were prepared with 5% corundum and the Rietveld method (Cheary and Coelho, 1994) used for quantitative analysis.

Water requirement was evaluated following EN 450-1 (BSI, 2012). A reference PC mortar (w/c ratio 0.5, cement to (standard) sand ratio 1:3) was prepared. A truncated conical mould was filled with the mixture and hand compacted (on the jolting table). Following removal of the mould and a fixed number of jolts, the mortar spread was measured. This was repeated for fly ash (30% in cement) mortars, with water contents adjusted to match the PC spread. The result is given as the percentage of water contents in PC/fly ash and PC mortars at equal flow.

Fly ash reactivity was assessed using activity index tests described in EN 450-1 (BSI, 2012), with standard mortars (w/c ratio 0.5). Six 40 mm × 40 mm × 160 mm prisms were cast for the PC/fly ash (25% in cement) and PC mortars and water cured at 20°C, with three tested in compression at both 28 and 90 days. The activity index is the percentage of PC/fly ash to PC mortar strengths at each age. Additional pozzolanic cement (lime consumption) tests were made selectively, based on EN 196-5 (BSI, 2011b) using PC/fly ash slurry.

SEM was carried out on the fly ashes using Hitachi S-4700 or Philips XL-30 instruments at accelerating voltages of 5 – 15 kV. The samples were prepared by depositing fly ash on a double sided 10 mm diameter adhesive tape/aluminium stub and coated with a 25 nm layer of Pd-Au alloy.

Concrete Properties

PC and fly ash (30% in cement) concretes with w/c ratios of 0.45 and 0.55 and fine/total aggregate ratios of 0.42 and 0.44 were tested, see Table 2. They were prepared following BS 1881-125, (BSI, 2013a) with the SP dose, added to achieve a target slump of 100 to 150 mm, i.e. S3 to EN 206 (BSI, 2013b), providing a measure of fly ash effects on fresh properties. Compressive strength (2 or 3 x 100 mm cube specimens at each age) was measured after water curing at 20°C up to 180 days. Concretes with fly ash where water savings were possible (i.e. S3 slump, using the same SP dose as for PC and 10 to 15 l/m³ water reductions) were also tested for compressive strength (w/c ratio 0.55).

RESULTS

Fly Ash Characteristics

Fineness and loss-on-ignition

The fly ash fineness and LOI results are given in Figure 1, which also shows median particle sizes, and specific surface area and foam index values. The reference fly ashes, FA1 to 3, had fineness between 9.6 and 32.8% (retained on the 45 µm sieve) and median particle sizes from 12.1 to 28.2 µm. Their LOIs were between 4.0 and 5.9%, with specific surface area and foam index values from 1.7 to 2.3 m²/g and 100 to 160 µl. The materials, therefore, met fineness (Category N ≤ 40%) and LOI (Category C ≤ 9.0%) requirements of EN 450-1 (BSI, 2012).

The NO_x reduction fly ashes (SCR and SNCR) FA4 and 5 had fineness of 12.1 and 15.1%. It is also evident that these had relatively low median particle size, LOI, specific surface area and foam index values. Fly ash from in-

combustion NO_x reduction FA6, however, was coarser than these and FA1 and 2. In addition, while it had a slightly higher LOI than the other materials, its specific surface area and foam index values were noticeably greater. Again, the materials all met EN 450-1 (BSI, 2012) requirements for the two properties covered.

The co-combustion fly ashes, FA7 to 9, were among the coarsest tested, 24.4 to 29.4%, with median particle sizes, 29.7 to 34.0 μm , and LOIs, 9.8 to 17.3%. FA7 and 8 were from anthracite coal, which can affect LOI (Sear, 2001; Porle and Parker, 2012), irrespective of co-combustion and may also be influenced by collection time (summer/winter). While FA7 and 8 had relatively high specific surface area and foam index values, these were lower for FA9. All fly ashes met EN 450-1 (BSI, 2012) fineness requirements, but exceeded the LOI limit.

The supercritical fly ashes, FA10 and 11, had fineness of 20.0 and 29.6%, while this was 19.1% for the oxy-fuel fly ash. The LOI, specific surface area and foam index values of FA10 and 11 were some of the lowest measured, i.e. 2.4 and 1.4%, 1.8 and 0.8 m^2/g , and 100 and 20 μl respectively, suggesting good characteristics for air-entrainment, while FA12 was in the mid-range for these. The fly ashes again met EN 450-1 (BSI, 2012) requirements (for the two main properties).

Appearance

In general, most fly ashes, given their dry condition, were free flowing powders, however, the co-combustion materials appeared granular and less cohesive than the others. The colour test results, as lightness values, are given against LOI in Figure 2. The data indicate that lightness decreased with increasing LOI, however, while there was a noticeable reduction with LOI up to about 7.0%, small changes were obtained thereafter. Between fly ashes, those from NO_x reduction (post-combustion) and supercritical technologies were lightest, while the in-combustion NO_x reduction, and co-combustion materials were darkest. Fly ash colour can be affected by iron in the material (Concrete Society, 2011) and this may also have influenced the results.

Bulk oxide and mineralogy

The bulk oxide composition and mineralogy of the fly ashes are given in Tables 3 and 4. These indicate that all fly ashes were low lime (< 5.0%). While there were some differences in major oxides, e.g. silica and alumina were lower in co-combustion and supercritical fly ashes respectively, with iron oxide higher for petroleum coke (co-combustion) and oxy-fuel combustion, most met the main oxide requirement of $\geq 70\%$ in EN 450-1 (BSI,

2012), except FA10 and 11 (supercritical), which were slightly below this. In general, sulfate levels were $< 1.5\%$, with higher values for petroleum coke (FA9) and oxy-fuel combustion (FA12; greater than the 3.0% limit in EN 450-1 (BSI, 2012)) noted. The fly ashes were all within the Standard's limit for alkalis (sodium oxide equivalent $\leq 5.0\%$).

The fly ash mineral compositions are also shown in Tables 3 and 4. For the reference fly ashes, quartz was from 8.6 to 11.1% and mullite 10.4 to 15.6%, with hematite 2.2 to 3.2%. For the modern fly ashes, the values were 3.9 to 20.7%, 5.6 to 17.9% and 1.4 to 4.5%. While there was some agreement between bulk oxide and mineral compositions with those of earlier studies (Dhir et al., 1996), in a few cases (e.g. quartz in FA4 and FA6 and quartz/mullite in FA12), differences were noted. However, it was not possible to relate these to the coal-fired power technologies. Estimates of amorphous glass (glass/others by difference of crystalline contents/LOI) are given in the tables. These ranged from 66.5% to 73.2% and 59.2 and 83.8% for reference and modern fly ashes, which is also similar to those found previously.

Water requirement and reactivity

The water requirement results are given in Figure 3, against fly ash fineness, which shows general agreement between the properties, with fine and/or low LOI fly ashes giving values between 93 to 98% of PC, including finer reference (FA1 and 2), NO_x reduction (FA4 to 6) and supercritical steam (FA10 and 11) materials. Of these, only the reference fly ashes were $\leq 95\%$, i.e. EN 450-1 (BSI, 2012) limit for Category S material. Where fineness (45 μm sieve retention) exceeded 20%, most water requirements were around 100% or more, with highest values between 103 and 105% for co-combustion fly ashes (FA7 to 9).

The activity index results at 28 and 90 days are also given in Figure 3 against fly ash fineness and show that the materials met EN 450-1 (BSI, 2012) requirements ($\geq 75\%$ at 28 days, $\geq 85\%$ at 90 days). In addition, there was, as noted previously, a tendency for reduced activity index with coarser fly ash, with a similar trend line gradient at both ages. At 90 days, most fly ashes had activity index values $> 100\%$, with the reference, (FA1 to 3), NO_x reduction (FA4) and co-combustion (FA7) materials giving slightly higher values.

Further tests were made on selective fly ashes using the pozzolanic cement (lime consumption) test, based on EN 196-5 (BSI, 2011b), with 25% fly ash, and have been reported elsewhere (McCarthy et al., 2017). Of the materials

investigated (FA1, 4, 5, 7, 8, 10 and 11), all passed by 8 days, i.e. were below the lime saturation line, except FA11, which achieved this at 15 days, suggesting suitability of these as pozzolanic cements (at this fly ash level).

Concrete Properties

Superplasticizing admixture demand

The SP doses to achieve slump between 100 and 150 mm were all between 0.30 and 0.85% by mass cement (recommended limits: 0.25 to 1.00%), as shown in Figure 4, where the results are compared with fly ash fineness. These suggest a tendency for increasing SP dose requirements with coarser fly ash, particularly when the fineness was greater than 20%. It was also noted that FA6 and FA8, had the highest dose requirements at both w/c ratios (0.45 and 0.55), exceeding those of PC (0.60% for both w/c ratios) by between 0.15 and 0.25%.

The NO_x reduction fly ash concretes, except FA6 (0.80 and 0.85% by mass cement), had SP doses between 0.30 to 0.45% by mass cement. Doses were relatively high for the co-combustion fly ashes at both w/c ratios, 0.55 to 0.80%, with FA7 lowest and FA8 highest of these. The supercritical fly ashes had SP doses between 0.60 to 0.70%. These had fineness (20.0 and 29.6%) similar to the co-combustion fly ashes (24.4 to 29.4%), however, they gave some differences with regard to SP dose, probably reflecting their LOI. The oxy-fuel fly ash had SP doses of 0.70 and 0.75%, which is reasonable given its fineness.

Compressive strength

Compressive strength development for the fly ash concretes at 0.45 and 0.55 w/c ratio are shown in Figure 5. These follow typical behaviour, increasing with time at a reducing rate until the end of the tests. In general, FA1 (Category S fly ash) concrete had highest compressive strength at the two w/c ratios and various test ages for the reference fly ashes, with FA2 and 3 up to about 5.0 MPa lower than this from 28 days.

Little effect was observed between compressive strengths of NO_x reduction fly ashes (post and in-combustion), with differences up to about 2.0 to 3.0 MPa, noted over the test ages and two w/c ratios. This type of behaviour was also found for co-combustion fly ash, with small variations, mainly in a similar range. The supercritical and oxy-fuel fly ash, FA10 to 12, concretes gave minor differences in early strength and slightly greater effects at later ages, with the ranking generally changing between materials and w/c ratios. At 28 and 90 days, the ranges for all fly ashes were 4.0 to 5.0 MPa and 5.0 to 6.0 MPa at 0.45 and 0.55 w/c ratio respectively. While FA1

always had highest strength and there was a tendency for the results to follow fineness, no consistent effects for the different fly ashes were noted.

The fly ashes for the water-reduced concretes were those requiring less SP than PC (FA1, 2, 4 and 5). Using the SP dose for PC concrete, a water reduction of 15 l/m³ was achieved in the fly ash concretes, except FA2, where this was 10 l/m³. Compressive strengths up to 180 days for these are shown with equal w/c ratio concretes in Figure 6. As indicated, increases of 2.0 to 7.0 MPa over the test age range were obtained with water savings compared to the fixed w/c ratio fly ash concretes. FA1 had highest compressive strengths at 28, 90 and 180 days, while FA2 was lowest, influenced by its greater w/c ratio. It is interesting to note that the fly ash strength profiles tended to mirror those of PC, with both concrete types showing continued increases during testing and little closure between these by the end of the test period.

DISCUSSION

Fly Ash Characteristics

Two of the main factors associated with coal-firing influencing the properties of fly ash and its behaviour are (i) the characteristics and preparation of coal and (ii) the combustion conditions (Sear, 2001; Spliethoff, 2010). Given the power technologies being examined, it may be expected that those affecting the fuel composition, e.g. co-combustion; or combustion process, e.g. oxy-fuel combustion would have greater effects on fly ash, while those using processes following this, e.g. post-combustion NO_x reduction, might have less. To assist the interpretation, SEM studies were carried out and are evaluated in this section, see Figure 7.

The SEM images for the reference fly ashes indicate that these materials mainly comprised spherical, smooth-surface particles, covering a range of sizes and were generally free of carbon and scoria. Similarly, their chemistry was typical of what may be expected for the coal type (Sear, 2001). It is reasonable that the finer of these materials exhibits good water-reducing properties and reactivity, with reduced benefits as the quantity of larger particles increases.

While chemicals, such as ammonia, are injected for NO_x reduction methods (post-combustion), this is unlikely to affect fly ash properties, although their release could be an issue during concrete manufacture (Sear and Guest, 2012; Rathbone and Robl, 2002). The properties found for FA4 and FA5 are, therefore, likely to relate to the

main operating conditions at the power station. The SEM images for these were similar to the reference fly ashes and confirm the high fineness/low LOI for the materials. This was also generally seen in the water requirement and reactivity tests, and specific surface area and foam index values. With in-combustion NO_x reduction, the fineness and LOI obtained may reflect the combustion conditions. Previous work (Hower et al., 1997; Fox and Constantiner, 2007) suggests increased coarsening of fly ash/carbon content, after retro-fitting power stations with low NO_x burners. The SEM images indicate partially melted/rough surfaces, and scoria/carbon particles were present. The above effects and slight reductions in silica and alumina compared to other materials, did not seem to affect reactivity, as suggested by activity index.

FA7 and 8 were from anthracite coal, which is likely to influence properties, and ammonia was also added which may have similar effects to those for NO_x reduction (Sear and Guest, 2012). The characteristics of co-combustion fly ash can be related to the fuel properties and combustion process (Sarabèr, 2012). Studies suggest the material is of similar size / size range to coal ash, with morphology tending to be more or less spherical, agglomerated or irregular (Kalembkiewicz and Chmielarz, 2012; Sarabèr, 2014). The SEM images in Figure 7 indicate small crystals on particle surfaces, with some clusters, and scoria/carbon present, which are also reflected in the water requirement and activity index results, particularly the former. The main oxide results may be due to coal dilution, while high sulfate in FA9 is likely to be from the co-fuel (Alhajibrahim and Morsi, 1992). The various factors influencing LOI mean this may either increase or decrease with co-combustion (Kalembkiewicz and Chmielarz, 2012; Sarabèr, 2014). Given the LOI of FA7 and 8, (likely to reflect coal type), the specific surface area and foam index values are reasonable. The relatively low values for the latter two with FA9 may relate to dense carbon, which has been noted previously with petroleum coke co-combustion fly ash (Scott and Thomas, 2007).

Supercritical steam fly ashes were of medium/high fineness and low LOI. The SEM images show that these comprised spherical particles of various sizes with clean surfaces, and some of irregular shape, which relate to their water requirements (< 100%) and medium/high activity index. The low carbon (and specific surface areas) obtained may be due to increased combustion efficiency/other processes used with this technology (e.g. degree of coal pulverising, carbon burn-off; Sato et al., 2001). The main oxide contents suggest possible co-combustion, but this is not known. The oxy-fuel fly ash was of medium fineness and LOI, with rough, partially crystallised particles, signs of agglomeration and some of irregular shape. As noted above, research suggests this fly ash can have similar properties to that produced during air combustion (Wall et al., 2009), while the high sulfate levels

found may reflect flue gas recycling (Schleffknecht et al., 2011), although as noted previously (Sarabèr, 2012) behaviour could also be influenced by the scale of the trial burner.

Concrete Properties

The benefits of fine, low LOI fly ash on fresh concrete are well established. Indeed, fly ash influences can include enhanced particle packing, releasing water and improving mix fluidity, as well as greater particle dispersion and lubricating action due to ‘ball bearing’ effects (Sun et al, 2003; Thomas, 2013). These and differences in irregular and porous particles between materials, are likely to influence the concrete results. Research from the 1980s (Dhir et al., 1985) gave general agreement between water requirement (in mortar) and concrete for equal slump. Comparable behaviour for SP dose to achieve the target slump was noted with the modern fly ashes, see Figure 8(a). The 1980s research also found that fly ashes of equal water requirement may not give the same slump in concrete and similar type effects occurred in the current study. For example, in-combustion NO_x reduction FA6, Figure 8(b), had high specific surface area (which mainly corresponds to unburnt carbon (Külaots et al., 2004)) and SP dose, but low water requirement. Although several factors can affect the SP dose (Termkhajornkit and Nawa, 2004), the results suggest take up of the admixture by carbon.

While the physical and chemical properties of fly ash are known to affect concrete strength, it is the former (in terms of fineness) which has been found to give stronger relationships (Dhir et al., 1996; McCarthy et al., 2013). In order to examine this for the modern fly ashes, the 28 and 90 day cube strength data are given in Figure 9, against fineness parameters. The results indicate gradual reductions in compressive strength at 28 and 90 days with increasing 45 µm sieve retention and slightly greater effects at the later test age. Similar behaviour was also noted with the sub-10 µm content present in fly ash, considered to be the reactive component in the material (Gambhir, 2013). The results from the 1990s study (single and between-source fly ashes) are also shown in the figure, which indicate similar trends for the data and general agreement between studies.

Overall, the research suggests that coal-fired power technologies can have some effects on fly ash properties, particularly those modifying the fuel or combustion conditions and in some cases the use of beneficiation techniques may be appropriate. However, the behaviour of the fly ashes, generally follows that noted previously for the material, e.g. effects of fineness and LOI on fresh and hardened concrete properties.

A comparison is made of the variability in 28 day strength results over a 20% fineness range for fly ash concretes of similar w/c ratio using data from the 1990s (Dhir et al., 1996) and current studies in Table 5. These indicate that the variability in strength for the modern coal-fired power techniques, from a range of sources, compares favourably with that of the earlier study.

CONCLUSIONS

Characterization tests suggest that modern technologies used in coal-fired power generation can influence the properties of fly ash produced. In general, techniques affecting the fuel and combustion process, i.e. in-combustion NO_x reduction, co-combustion and oxy-fuel combustion (trial burning unit) tended to give coarser fly ash of high LOI (and specific surface area). For fly ash from supercritical steam, lower carbon contents (and specific surface area) were obtained. Fly ash from methods used following combustion, i.e. post-combustion NO_x reduction, seem to be less affected.

Some differences in chemical composition were found between the fly ashes, e.g. silica and alumina contents were less for co-combustion and supercritical steam fly ashes respectively, while sulfate levels were higher with petroleum coke and oxy-fuel combustion. However, in most cases, this was similar to previously published data, mainly meeting the requirements of EN 450-1 (BSI, 2012) and what would be expected for the types of coal used during electricity generation.

The effects noted above for the modern fly ashes were reflected in the water requirement, which generally increased with coarsening and LOI, with highest values for the co-combustion fly ashes. The reactivity, according to activity index tests, was less affected by these, with all fly ashes meeting the requirements of EN 450-1. Selective fly ashes were also found to pass the lime consumption pozzolanic cement test (based on EN 196-5, 2011) at the 25% level (in cement).

The SP doses to achieve a target slump in concrete tended to increase with coarsening and LOI of reference and modern fly ashes. Similar behaviour to that noted previously for fly ashes from the 1980s (between water requirements for mortar (following Standard methods) and concrete) was found between water requirement in mortar and SP doses in concrete for target slump in the current study. Increased SP doses tended to be required with increasing specific surface area of fly ash.

The 100 mm cube tests indicate similar early strengths between fly ash concretes. At 28 days and later test ages, compressive strength was slightly greater in concretes with finer material. Comparisons with a study on fly ashes from the 1990s indicate similar trends. The results suggest that, although modern coal-fired power technologies can influence fly ash properties, they follow established behaviour for the material. Further studies investigating other aspects of the fly ashes and their use in concrete have been carried out and will be reported on in due course.

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Table captions

Table 1 Summary of fly ashes

Table 2 Mix proportions of test concretes

Table 3 Bulk oxide and mineral compositions of reference fly ashes

Table 4 Bulk oxide and mineral compositions of fly ashes from modern coal-fired power technologies

Table 5 Variations in 28 day concrete strength for $\approx 20\%$ fly ash fineness range from different studies

Table 1 Summary of fly ashes

CODE	DESCRIPTION
FA1	Category S from base load station
FA2	Category S
FA3	Produced during the 1990s
FA4	From station with Selective Catalytic Reduction (SCR)
FA5	From station with Selective Non-Catalytic Reduction (SNCR)
FA6	From station with a natural gas re-burn system converting NO _x to nitrogen and water
FA7	Co-combustion (woodchip) sampled in winter
FA8	Co-combustion (woodchip) sampled in summer
FA9	Co-combustion (10% petroleum coke)
FA10	From station with supercritical steam generator
FA11	From station with supercritical steam generator
FA12	From oxy-fuel combustion using a trial burner unit

Table 2 Mix proportions of test concretes

MIX	W/C RATIO	CONCRETE MIX PROPORTIONS ¹ , kg/m ³								Total
		Free water	Cement / Addition			Aggregate				
			PC	Fly ash	Total	Sand	4/10	10/20	Total	
PC										
1	0.45	165	365	0	365	790	380	710	1880	2410
2	0.55 ²	165	300	0	300	850	380	705	1935	2400
Fly Ash										
1	0.45	165	255	110	365	775	375	695	1850	2380
2	0.55 ²	165	210	90	300	845	375	695	1915	2380

¹ Superplasticizer used in quantities necessary to achieve Slump Class S3

² Water reducing mixes were carried out at 0.55 w/c

Table 3 Bulk oxide and mineral compositions of reference fly ashes

CHARACTERISTIC	FLY ASH		
	FA1	FA2	FA3
Bulk oxide composition, %			
CaO	3.01	2.31	4.03
SiO ₂	48.39	49.81	43.40
Al ₂ O ₃	20.12	22.31	23.28
Fe ₂ O ₃	8.35	7.94	11.01
MgO	1.60	1.49	1.81
MnO	0.06	0.05	0.08
TiO ₂	1.03	1.13	1.10
K ₂ O	2.80	3.42	2.67
Na ₂ O	2.01	1.33	1.71
P ₂ O ₅	0.46	0.23	0.54
SO ₃	0.97	0.89	1.40
Na ₂ O Equivalent	3.85	3.58	3.47
Mineral composition, %			
Quartz	9.8	11.1	8.6
Hematite	2.2	2.3	3.2
Magnetite	0.1	0.2	0.1
Mullite	10.4	11.0	15.6
Glass/Others ¹	73.2	71.5	66.5

¹ not including LOI

Table 4 Bulk oxide and mineral compositions of fly ashes from modern coal-fired power technologies

CHARACTERISTIC	FLY ASH								
	FA4	FA5	FA6	FA7	FA8	FA9	FA10	FA11	FA12
Bulk oxide composition, %									
CaO	1.91	3.74	1.64	3.55	2.94	4.63	4.47	4.19	4.20
SiO ₂	51.42	47.07	45.74	42.86	41.98	39.41	43.97	44.43	47.70
Al ₂ O ₃	17.34	19.93	16.55	20.92	20.82	21.07	16.34	16.00	20.08
Fe ₂ O ₃	8.96	9.13	7.72	6.71	8.15	12.99	7.89	8.49	12.49
MgO	1.60	1.66	1.09	1.09	1.17	1.40	1.38	1.37	1.41
MnO	0.06	0.09	0.04	0.12	0.09	0.13	0.05	0.05	0.07
TiO ₂	0.96	1.07	0.83	0.98	0.94	1.03	0.81	0.87	1.11
K ₂ O	2.04	3.37	1.73	1.55	2.05	2.52	1.79	1.90	2.47
Na ₂ O	1.74	1.44	1.24	0.84	0.75	1.19	1.69	2.88	1.50
P ₂ O ₅	0.23	0.84	0.15	0.89	0.86	0.56	0.43	0.29	0.13
SO ₃	1.45	1.24	1.08	0.8	1.24	2.55	0.74	0.91	3.39
Na ₂ O Equivalent	3.08	3.66	2.38	1.86	2.10	2.86	2.87	4.13	3.09
Mineral composition, %									
Quartz	20.7	11.1	19.0	3.9	4.8	7.0	5.6	10.7	12.8
Hematite	2.4	2.7	1.7	1.4	1.5	2.6	2.4	3.0	4.5
Magnetite	0.1	0.2	0.1	0.1	0.2	0.4	0.2	0.2	0.1
Mullite	7.6	8.8	10.6	9.5	11.8	11.9	5.6	6.2	17.9
Glass / Others ¹	66.6	73.8	61.3	71.4	64.4	68.3	83.8	78.5	59.2

¹ not including LOI

Table 5 Variations in 28 day concrete strength for $\approx 20\%$ fly ash fineness range from different studies

STUDY/ FLY ASH SOURCES	CONCRETE ¹ W/C RATIO	FINENESS ² RANGE	NUMBER OF MIXES	NUMBER OF FLY ASHES	NUMBER OF SAMPLES	COEFFICIENT OF VARIATION, %
<u>Dhir et al., (1996)</u>						
Between sources	0.50	7.5 – 27.0	2	4	16	6.7
Within source	0.50	6.0 – 25.5	2	5	20	5.3
Within source	0.50	2.0 – 22.0	2	5	20	5.6
<u>Current</u>						
Between sources	0.45	9.1 – 32.8	1	12	33	4.2
Between sources	0.55	9.1 – 32.8	1	12	33	5.1

¹ Fly ash level in cement – 30%² 45 μm sieve residue, %

Figure captions

Figure 1 (a) Fineness and (b) Loss-on-ignition and associated properties of fly ashes

Figure 2 Relationship between loss-on-ignition and colour (lightness value) of fly ashes

Figure 3 Relationships between fineness (45 μm sieve residue) and water requirement/activity index of fly ashes

Figure 4 Relationship between fineness (45 μm sieve residue) and SP dose (% by mass cement) of fly ash concretes (a) 0.45 and (b) 0.55 w/c ratios

Figure 5 Strength development (100 mm cube) of (a) reference, (b) NO_x reduction, (c) co-combustion and (d) supercritical and oxy-fuel fly ash concretes (0.45 and 0.55 w/c ratios)

Figure 6 Strength development (100 mm cube) of selective (a) water saving and (b) equal w/c ratio (0.55 w/c) fly ash concretes in comparison to PC

Figure 7 Scanning electron microscopy images of selective fly ashes

Figure 8 Relationship between (a) water requirement and (b) specific surface area of fly ash and SP dose (% by mass cement) of concrete (0.55 w/c ratio)

Figure 9 Comparison of (a) fineness (45 μm sieve residue) and (b) quantity of sub-10 μm particles against compressive strength; and (c) data from 1990s study (Dhir et al., 1996)

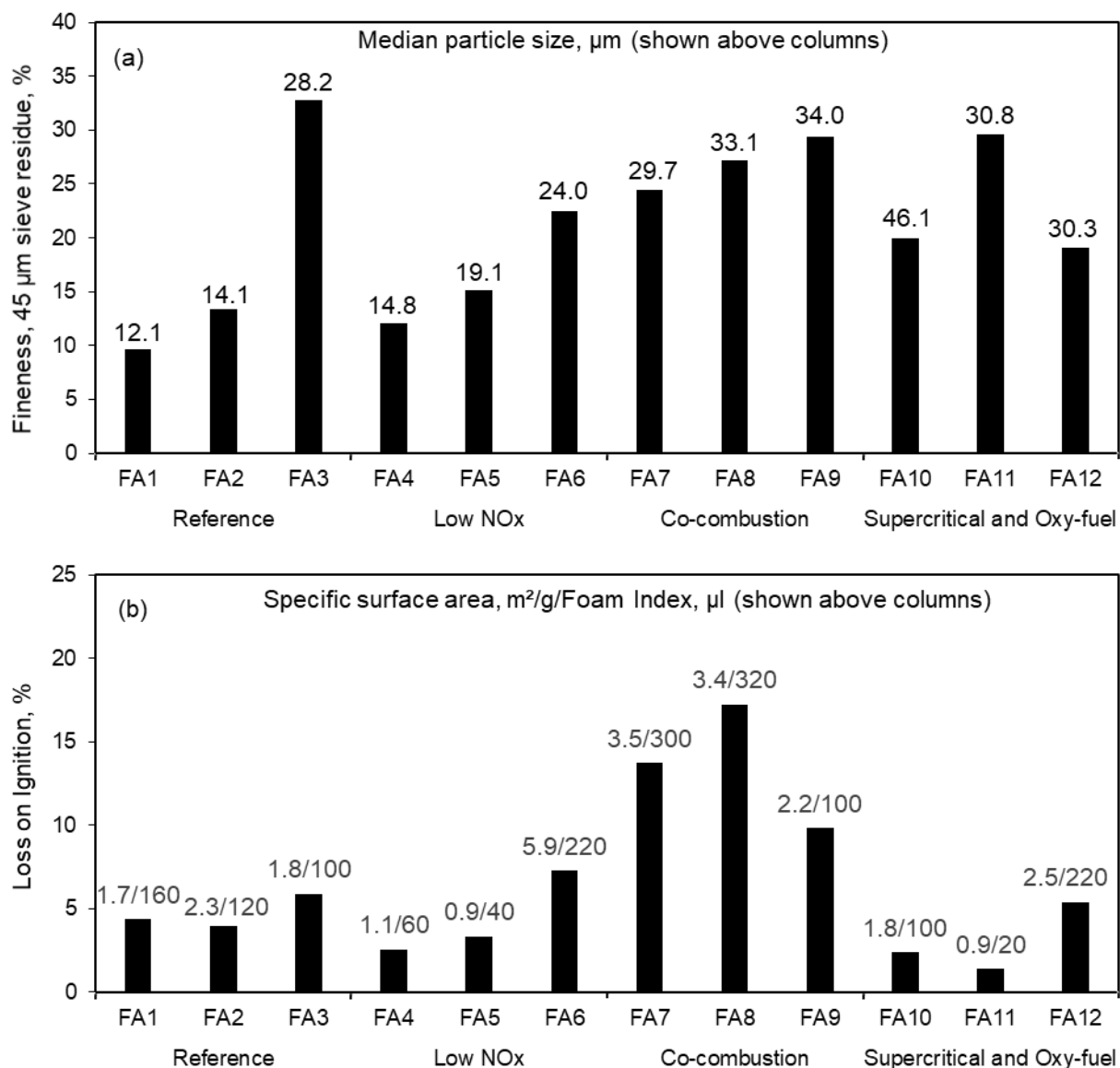


Figure 1 (a) Fineness and (b) Loss-on-ignition and associated properties of fly ashes

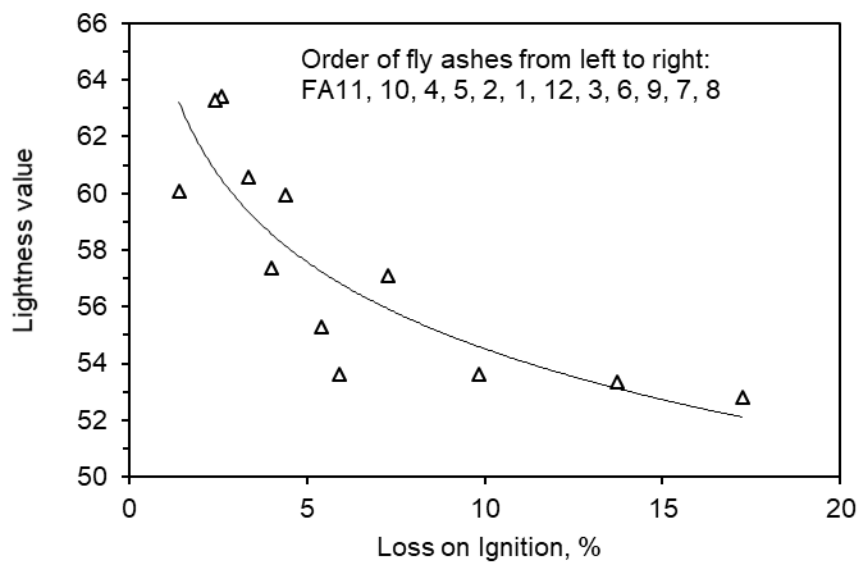


Figure 2 Relationship between loss-on-ignition and colour (lightness value) of fly ashes

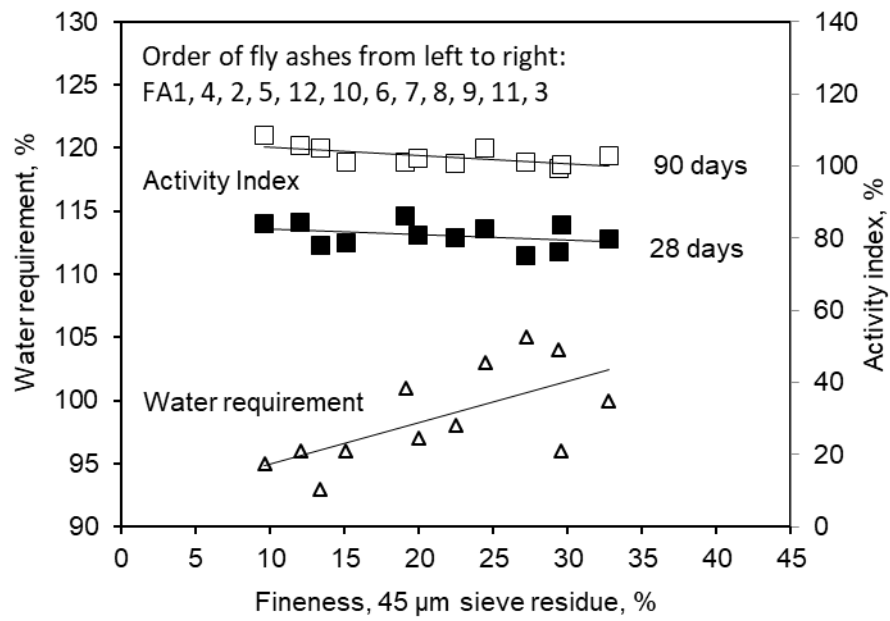


Figure 3 Relationships between fineness (45 µm sieve residue) and water requirement/activity index of fly ashes

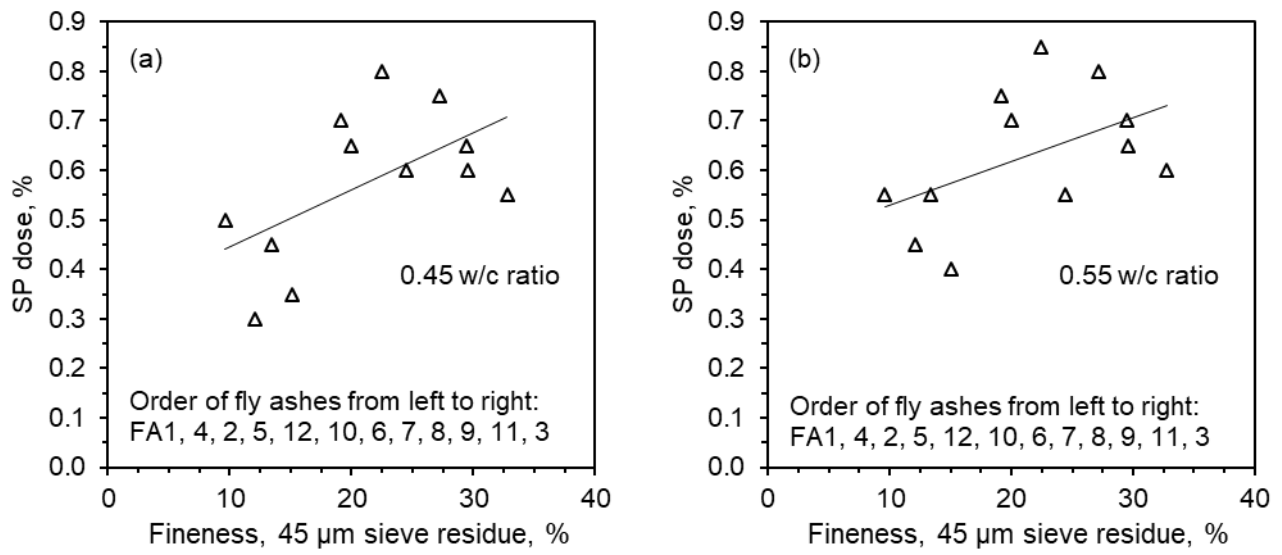


Figure 4 Relationship between fineness (45 µm sieve residue) and SP dose (% by mass cement) of fly ash concretes (a) 0.45 and (b) 0.55 w/c ratios

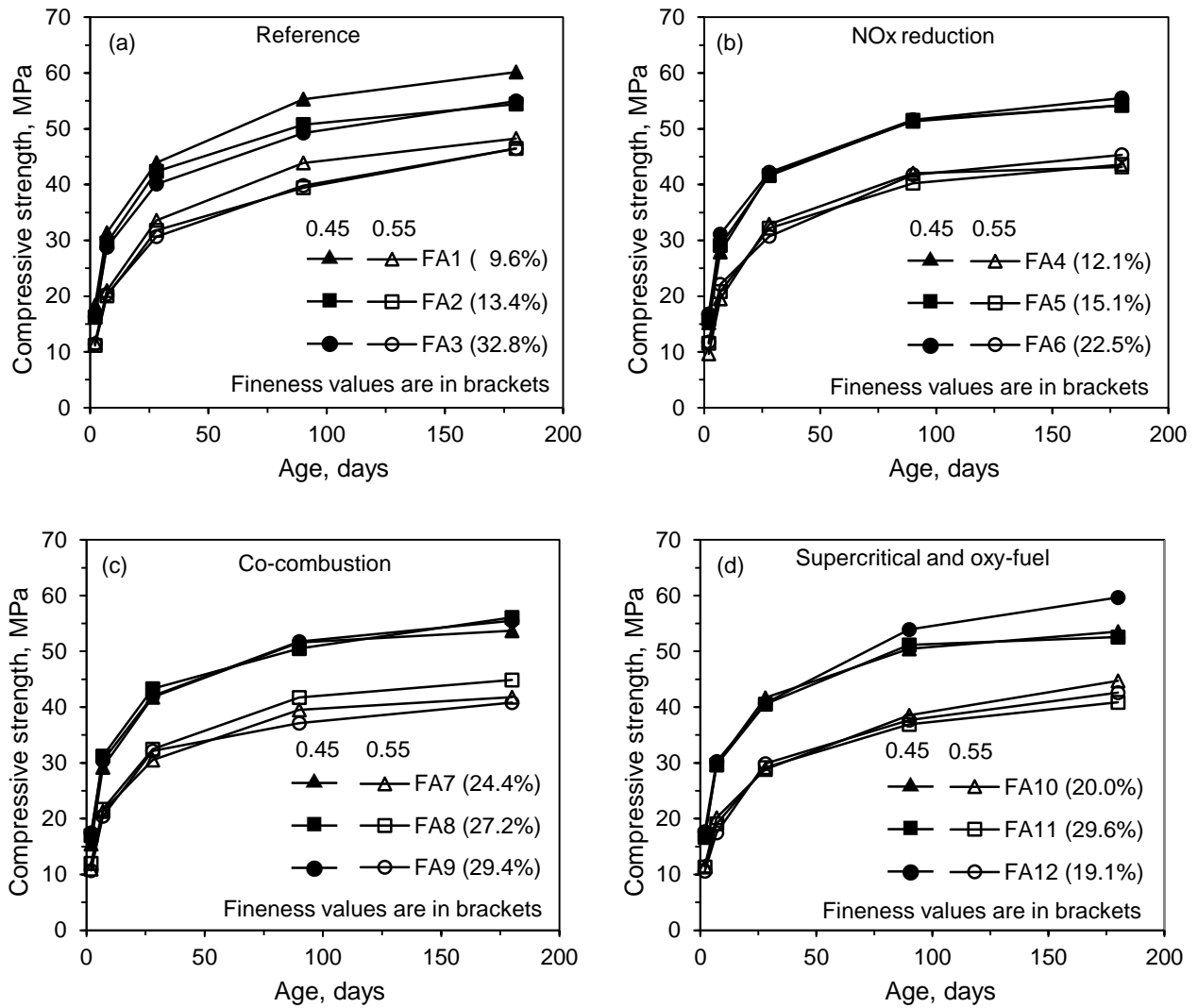


Figure 5 Strength development (100 mm cube) of (a) reference, (b) NOx reduction, (c) co-combustion and (d) supercritical and oxy-fuel fly ash concretes (0.45 and 0.55 w/c ratios)

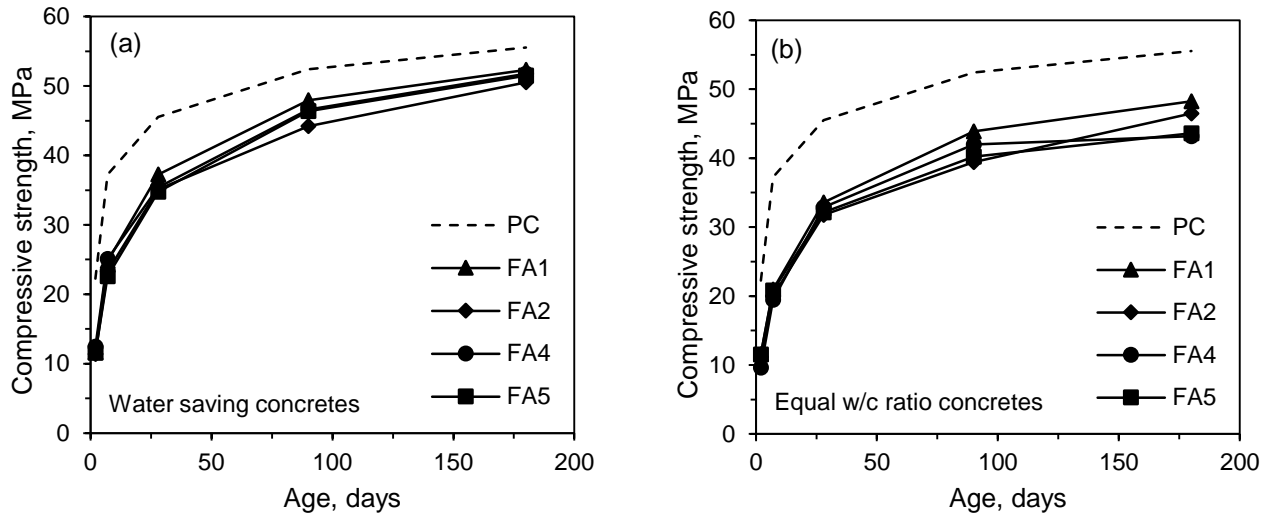
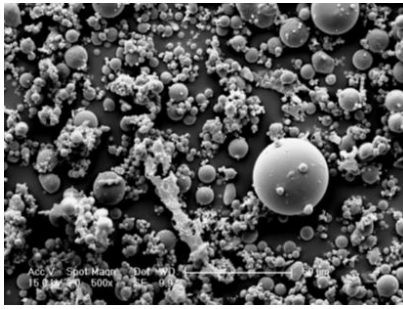
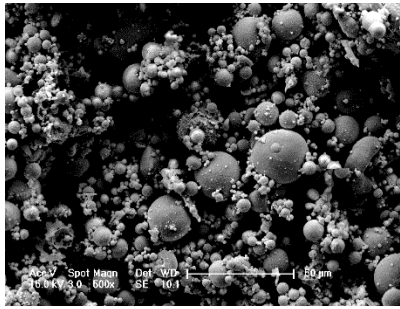


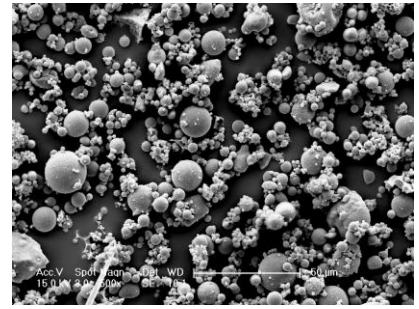
Figure 6 Strength development (100 mm cube) of selective (a) water saving and (b) equal w/c ratio (0.55 w/c) fly ash concretes in comparison to PC



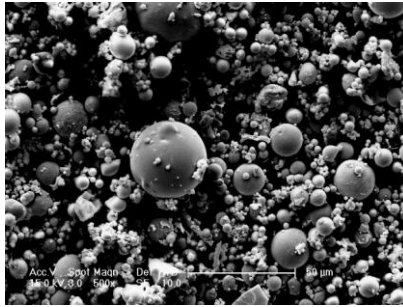
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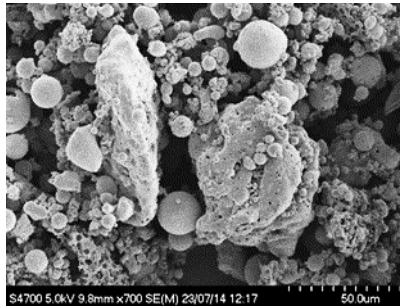
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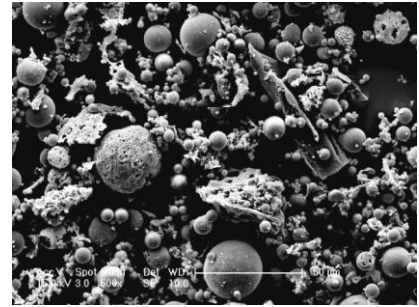
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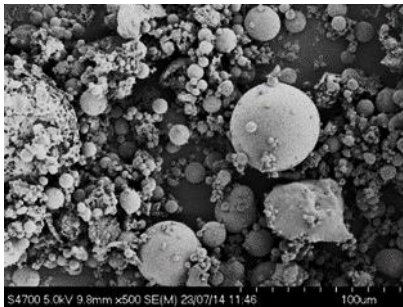
FA5



FA6



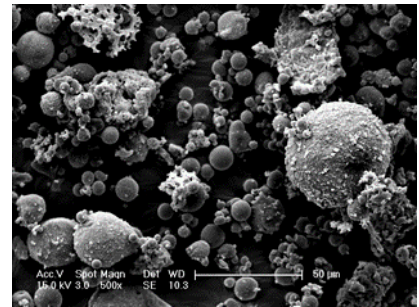
FA8



FA9



FA11



FA12

Figure 7 Scanning electron microscopy images of selective fly ashes

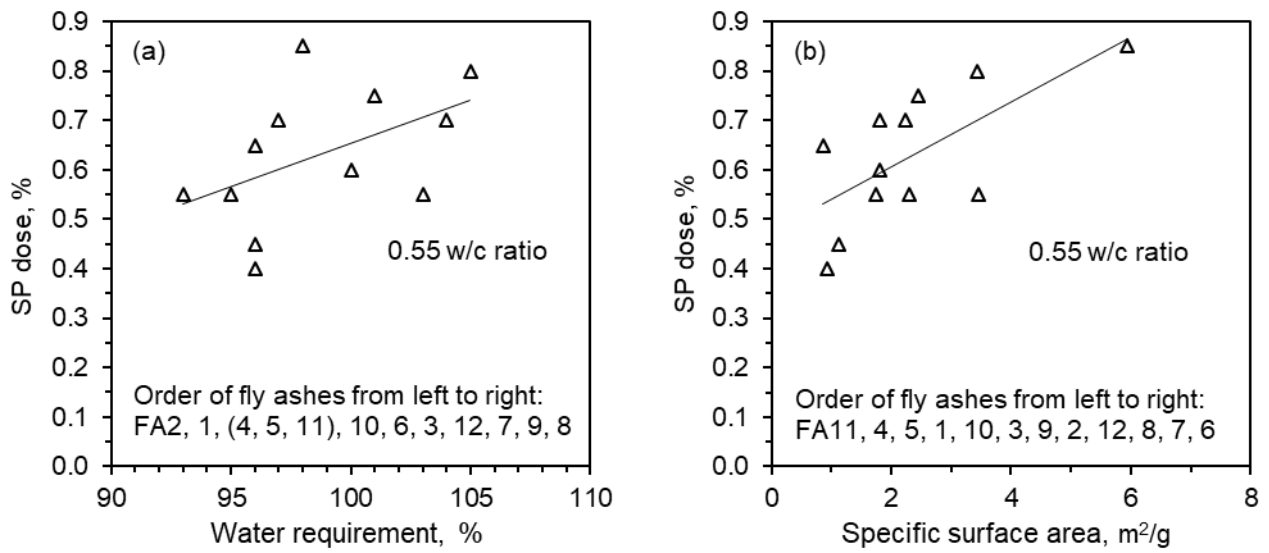


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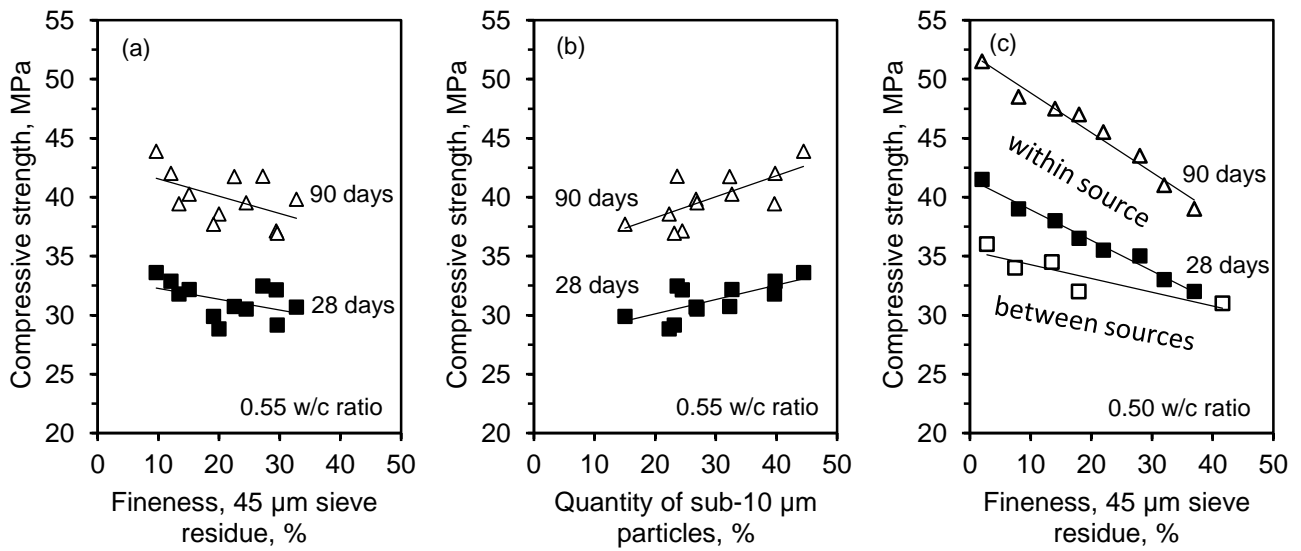


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